

Ab-Initio Cluster Calculations of Hole Transport and Activator Excitation in CsI:Tl and CsI:Na

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Abstract

We describe methods for using Gaussian94 (an *ab-initio* molecular orbital program) to compute energies and electron distributions that describe (1) the formation and transport of excess electrons and holes in the crystal CsI, (2) electron and hole capture by Tl and Na activator atoms, and (3) the electronic nature of the excited state of Tl and Na after the capture of an electron and a hole. To model these processes, the Schrödinger equation was solved at the Hartree-Fock level (in some cases with Møller-Plesset second-order electron correlation corrections) for clusters of 12 Cs and 20 I atoms and of 16 Cs and 29 I atoms in an electrostatic field generated by approximately 5800 point charges. We show that a relaxed hole in CsI is shared equally by two bound I atoms (classic V_k center) and that the predicted energy barrier for the motion of the hole is 0.15 eV. The transition state consists of the hole on a single I atom. We also show that a Na atom can capture an electron (but not a hole) and then trap a hole in its vicinity to form an impurity trapped exciton. On the other hand, a Tl atom binds a hole and then captures an electron to form an excited Tl atom. We believe that it is now computationally possible to model carrier transport and activator excitation in a variety of compounds to guide the search for new scintillators.

INTRODUCTION

This work is motivated by the need for better scintillators for gamma ray detection in medical imaging. Here we explore the feasibility of making qualitative predictions of the scintillation efficiency of host/activator combinations using *ab-initio* molecular orbital cluster computations. We stress several critical processes, such as electron and hole transport in the host, and the sequential capture of electrons and holes to form an excited state at or near an activator atom. For this we do not need high accuracy and do not attempt to predict spectroscopic properties.

Scintillation can be described in three stages [1] with an overall luminous efficiency (photons/MeV) given by

$$= S q$$

where n is the number of electrons and holes produced per MeV of ionizing radiation, S is the efficiency with which the electrons and holes transfer their energy to the luminescent center, and q is the quantum efficiency of the excited state of the luminescent center. We are interested in computing the transfer process in two separate, sequential steps: S_d —the diffusion of electrons and holes in the host crystal, and S_e —the production of an excited state by the sequential capture of an electron and a hole by an activator atom.

To validate the results, we use as a test material CsI [2], a scintillator of interest in both its pure and activated forms. In CsI:Na and CsI:Tl it is known that S_d and S_e are slow (~ 10 ns) but efficient processes and that a hole in the host CsI crystal creates a V_k center—a bound I_2^- molecule—aligned along the [100] axis.

COMPUTATIONAL METHODS

Program

The Gaussian94 program [3] at the Hartree-Fock (HF) and Møller-Plesset second-order perturbation theory (MP2) levels was used to determine energies and electron population distributions for clusters of atoms in a lattice of point charges. It was quickly found that the standard HF linear solution method was unable to converge for CsI clusters larger than about 15 atoms and hence the slower quadratic convergence method was used for all the results presented here. Atomic relaxation was performed using the numerical Fletcher-Powell method because the more efficient analytic methods are disabled when using point charges. Atomic charges and electron populations were determined from the Natural Population Analysis (NPA) phase of the Natural Bond Orbital (NBO) Analysis [4]. Excited states were treated using configuration interaction for single excitations (CIS).

The Gaussian94 runs were performed on a Silicon Graphics, Inc. Power Challenge computer with two R10000 processors and on a Cray J-90 at the National Energy Research Supercomputer Center at LBNL.

Effective Core Potentials and Basis Functions

The relativistic effective core potentials from the Los Alamos LanL2DZ basis set were used for the Cs, I, and Tl atoms. The basis functions for Cs were quite numerous and out of proportion to the simpler I basis functions and thus were reduced. Basis functions for both the Cs and I atoms were optimized for the cluster Cs_2I_2 in 508 point charges. Diffuse s, p, and d basis functions were added to the central row of atoms

Crystal Field Potential

The electrostatic potential was computed using a radially balanced Cs_4I_4 unit cell. This unit cell has zero dipole moments $q_i x_i$, $q_i y_i$, $q_i z_i$ and is radially balanced in the sense that if the distance from any point to the i th unit cell point charge is r_i , then $q_i r_i^2 = 0$. Even a small array of these unit cells gives excellent agreement between the Ewald sums and the site potentials for the central atoms. A $9 \times 9 \times 9$ array of Cs_4I_4 unit cells was used which yielded errors in the potential of the order of 10 mV rms. Additional adjustment of outer atoms to nearby vacant sites was used to further reduce the error to a few mV rms.

HOLE FORMATION IN THE CLUSTER $\text{Cs}_{12}\text{I}_{20}$

To model hole formation in CsI, we used the cluster $\text{Cs}_{12}\text{I}_{20}$ (see Fig. 1) in which two I atoms were surrounded by a sufficient number of atoms to create a realistic environment for motion in the x direction. In addition the four nearest Cs neighbors are allowed to move radially in the coulomb field of the hole. The coordinates of the six moveable atoms are $\text{I}_2(-a,0,0)$, $\text{I}_3(a,0,0)$, $\text{Cs}_1(0,b,b)$, $\text{Cs}_2(0,-b,b)$, $\text{Cs}_3(0,b,-b)$, $\text{Cs}_4(0,-b,-b)$.

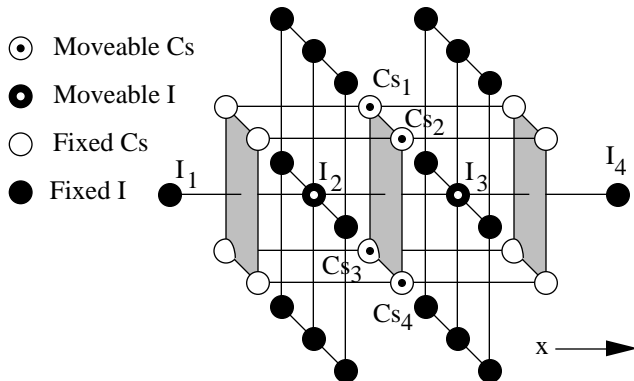


Figure 1. $\text{Cs}_{12}\text{I}_{20}$ cluster used to model hole formation in the CsI host crystal.

Ground State

Optimizing the variables a and b from their starting values of 2.284 Å reduced the ground state (neutral singlet) HF energy by only 0.4 mV. The variables also changed by only very small amounts: $a = 0.02$ Å, $b = -0.02$ Å. The electron population analysis (EPA) placed all electrons in the expected valence levels; all Cs charges were +1.00 and all I charges were -1.00.

Hole State

The HF calculation was repeated with a cluster charge one higher than the ground state (+1 doublet). The initial energy was 8.67 eV above the ground state. Optimizing a and b reduced the energy by 0.77 eV to 7.79 eV. The parameters for the relaxed configuration were $a = 1.73$ Å, $b = 2.47$ Å. Thus the central I_2 and I_3 moved together from an initial interatomic distance of 4.568 Å to 3.46 Å, and the four nearest-neighbor Cs atoms moved radially outward by 0.19 Å. The EPA showed that the I_2 and I_3 charges were both -0.54. The relaxed hole is therefore a bound I_2^- molecule, the expected V_k center.

Excess Electron State

The HF calculation was repeated with a cluster charge one lower than the ground state (-1 doublet). The energy increased by 0.19 eV and the EPA found that the negative charge was shared equally by I_1 and I_4 , the two most distant I atoms on the boundary of this particular cluster. The distribution of an excess electron depends on the details of the cluster; in smaller clusters we found the electron uniformly occupying Rydberg levels of all the atoms. We conclude that an excess electron is not localized and is not energetically bound by the cluster.

HOLE FORMATION AND TRANSPORT IN THE CLUSTER $\text{Cs}_{16}\text{I}_{29}$

To provide a large enough cluster to produce a V_k center on two symmetric sites, we used the cluster $\text{Cs}_{16}\text{I}_{29}$ with 11 moveable atoms (see Fig. 2) in which three I atoms were surrounded by a sufficient number of atoms to permit realistic motion in the x direction and in which the eight nearest Cs neighbors were allowed to move both along the x direction and radially in the coulomb field of the hole.

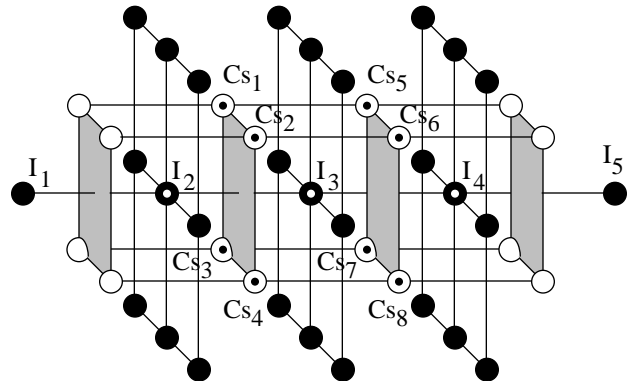


Figure 2. $\text{Cs}_{16}\text{I}_{29}$ cluster used to model hole formation and transport in the CsI host crystal. Atom symbols are the same as in Figure 1.

Hole State

Starting with the initial atomic configuration, a HF calculation was performed with a cluster charge one higher than the ground state (+1 doublet). The EPA revealed that the hole was mainly on I_3 , at the center of the cluster: $q_{I2} = -0.92$, $q_{I3} = -0.16$, $q_{I4} = -0.94$. A similar result has been reported for NaCl [5]. The energy was 8.36 eV above that of the ground state, similar to that of the $\text{Cs}_{12}\text{I}_{20}$ cluster.

Optimizing the seven variable coordinates reduced the energy by 0.85 eV to 7.51 eV, and resulted in the central I_2 and I_3 pulling together symmetrically from an interatomic separation of 4.568 Å to 3.5 Å while the four nearest-neighbor Cs atoms moved radially outward by 0.19 Å. The EPA found that the hole was shared by I_3 and I_4 : $q_{I2} = -1.00$, $q_{I3} = -0.41$, $q_{I4} = -0.62$. (The inequality of q_{I3} and q_{I4} is a manifestation of the asymmetry of the cluster used.) The relaxed hole is again a bound I_2^- molecule (V_k center).

Hole Transport:

Because a V_k center can be formed by either $\text{I}_2\text{-I}_3$ or $\text{I}_3\text{-I}_4$, depending on the x coordinate of I_3 , we explored how a V_k center can be shifted between the two sites by varying the x coordinate of I_3 from 0.0 to 1.2 Å in discrete steps of 0.2 Å. At each value of the x coordinate of I_3 , a ten-atom relaxation of the six parameters was performed. The x coordinates of I_2 , I_3 , I_4 and x_{hole} (the center of charge of the hole) are plotted in Fig. 3 as a function of the x coordinate of I_3 . Values for negative I_3 x coordinates were derived from the positive values by symmetry. Each six-parameter optimization required approximately 150 hours of computer time on the Power Challenge using two R10000 processors.

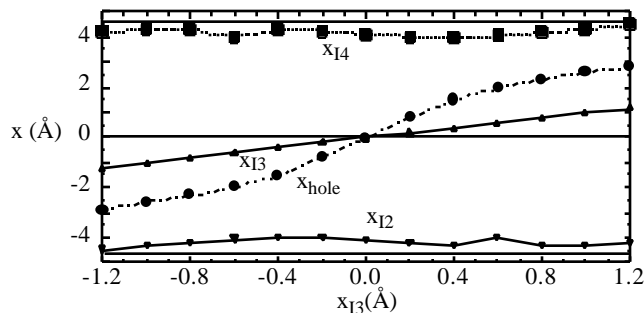


Figure 3. X coordinates of I_2 , I_4 , and x_{hole} (the center of charge of the hole) as the x coordinate of I_3 is varied.

In our previous work where only I_2 and I_4 were allowed to relax at each I_3 position, the HF energy vs. x_3 was almost perfectly flat. Figure 4 shows that some relaxation of the nearby Cs atoms is required to produce a stable V_k center at the HF level. Adding the effects of electron correlation using MP2, the binding of the V_k center increases. The importance of MP2 has also been shown for NaCl [5]. The results in Fig. 4 also show that the transition state for hole transport in CsI is an unstable one-center configuration that lies 0.15 eV above the relaxed V_k center configuration.

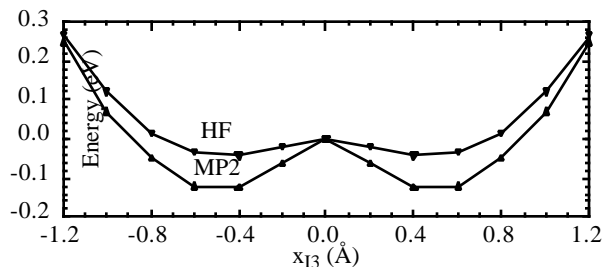


Figure 4. Energy at the HF and MP2 levels of theory as the x coordinate of I_3 is varied. The two stable configurations at $x_{I3} = -0.5 \text{ \AA}$ and $+0.5 \text{ \AA}$ are V_k centers at the I_2 - I_3 and I_3 - I_4 sites, respectively.

FORMATION OF THE EXCITED STATE OF CsI:Na

To model the formation of the excited state of Na in a CsI crystal, we used the $\text{Cs}_{12}\text{I}_{20}$ cluster with one of the Cs nearest the I_2 - I_3 site replaced with Na (see Fig. 5).

Ground State

The Na charge is +0.79 and the electronic orbital configuration is $3s(0.20)$, $3p(0.01)$. During relaxation the Na moves outward by 0.13 \AA and the energy drops 0.02 eV .

Hole State

Before relaxation, the energy is 8.60 eV higher than the ground state. Relaxation reduces the energy by 1.2 eV to 7.43 eV above the ground state. In addition, relaxation reduces the I_2 - I_3 distance, the Na atom moves radially outward by 0.54 \AA , and the Cs atoms move outward by about 0.2 \AA . The hole is located on atoms I_2 and I_3 which each have charge -0.50 . The Na charge is $+0.81$ and the electronic orbital configuration is

essentially unchanged from the ground state. Therefore the hole in CsI:Na appears identical to a V_k center in CsI. The Na atom acts as a spectator, moving outward in the coulomb field of the hole on I_2 - I_3 . It moves 0.36 \AA further than the other Cs atoms due to its smaller ionic radius.

Excess Electron State

The Na atom gains 0.91 electrons relative to the ground state, has a charge of -0.12 , and has an electronic configuration $3s(0.65)$, $3p(0.47)$. The energy is 0.09 eV below that of the ground state. Relaxation lowers the energy to 0.38 eV below the ground state and the Na atom moves outward by 0.54 \AA . The electronic configurations of the other atoms in the cluster are essentially the same as for the ground state. Therefore for this CsI:Na cluster an excess electron resides on the Na atom, is energetically bound to it, and the other atoms remain in their ground state.

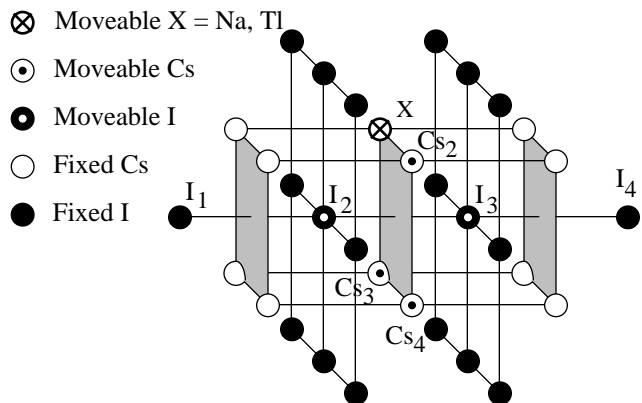
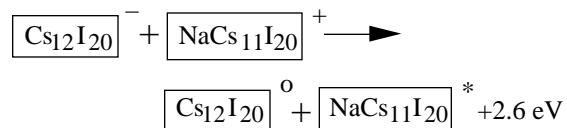


Figure 5: Cluster used to model hole and electron capture by Tl and Na atoms to form the excited state.

Excited State:

When the system is solved for the excited state (neutral triplet, using the CIS method), the energy is 4.81 eV above the ground state. Relaxation changes the atom coordinates and the energy by only a small amount. Relative to the ground state, the Na has gained 0.89 electrons and has an electronic configuration $3s(0.57)$, $3p(0.52)$ and the two nearest neighbor I atoms have each lost 0.51 electrons.

The preceding sections show that after ionizing radiation produces electron-hole pairs in CsI:Na, the electrons are captured by Na atoms while the holes form V_k centers. To determine whether it is energetically possible for a hole to be captured by a Na atom that had previously captured an electron, we computed the HF energies of the following four clusters and found that 2.6 eV was available for the reaction.



Thus Na is predicted to first capture an electron and then a hole to form an impurity-trapped exciton (Na^0 plus V_k center).

FORMATION OF THE EXCITED STATE OF CsI:Tl

The formation of the excited state of Tl in a CsI crystal, was modeled similarly using the $\text{Cs}_{12}\text{I}_{20}$ cluster with one of the Cs nearest the $\text{I}_2\text{-I}_3$ site replaced with Tl (Fig. 5).

Ground State

The Tl charge is +0.37 and the electronic orbital configuration is $6s(2.00)$, $6p(0.62)$, $7p(0.01)$. All eight nearest-neighbor I atoms have a charge of -0.93. All other Cs and I atoms have their nominal charges of +1.00 and -1.00, respectively. During relaxation the Tl moves outward by 0.05 Å and the energy drops 0.01 eV. These numbers are less than those for the case of Na in CsI:Na because Tl and Cs have more similar ionic radii.

Hole State

Before relaxation, the energy is 8.38 eV higher than that of the ground state. Relaxation reduces the energy by 0.04 eV and the atoms move very little (≤ 0.10 Å). The hole is located on a single I atom (one of the eight nearest-neighbors to Tl) with charge -0.07. The Tl charge is +0.33 and the electronic configuration is essentially unchanged from the ground state. As shown in Fig. 4, the one-center hole is only ~0.05 eV above the V_k center at the HF level. It is possible that the one-center hole configuration is favored because of its proximity to the relatively negative Tl atom whose charge of +0.37 represents a -0.63 charge defect relative to the Cs atoms in the lattice.

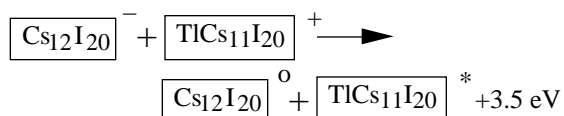
Excess Electron State

The Tl charge is +0.37 and the electronic configuration is the same as the ground state. The excess electron is shared equally by I_1 and I_4 , the two most distant I atoms, a situation essentially identical to that of the $\text{Cs}_{12}\text{I}_{20}$ cluster described earlier. Thus an excess electron in CsI:Tl is not localized, does not involve the Tl atom, and is not energetically bound.

Excited State

Using the CIS method, the excited state energy is 5.04 eV above the ground state. Relaxation changes the atom coordinates and the energy by only a small amount. Relative to the ground state, the Tl charge decreases by 0.17 to +0.20 and the excited electronic configuration is $6s(1.22)$, $6p(1.32)$, $7p(0.26)$ with the higher 6p and 7p orbitals gaining 0.95 electrons. All Cs and I atoms have essentially their ground state charges and electronic configurations.

After ionizing radiation produces electron-hole pairs, the holes in CsI:Tl are one-centered and bound near Tl atoms. To determine whether it is energetically possible for an electron to be captured by a Tl atom that had previously captured a hole, HF energies were computed for the following four clusters and it was found that 3.5 eV was available for the reaction.



Therefore the Tl first traps an hole and then an electron to form an excited Tl atom in a ground-state host lattice.

CONCLUSIONS

This work was intended as a feasibility study of what could be done with currently available software and hardware. We have demonstrated that it is now possible (although computationally intensive) to perform preliminary calculations of many of the critical processes in activated scintillators using molecular orbital cluster calculations. Clearly it would be desirable to continue this work using larger clusters of atoms in more complete states of relaxation, a larger number of basis functions, at the highest feasible level of theory, replacement of ground-state boundary atoms with pseudopotentials, and including spin-orbit coupling.

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